

LECTURE # 8

Introduction to Solvent Extraction

Solvent extraction technique is a part of analytical chemistry and has been recognized as an excellent separation method because of its ease, simplicity, speed, and wide scope. Utilizing apparatus no more complicated than a separating funnel, requiring just several minutes, at the most to perform, applicable both to trace and macro-levels of metals, extraction procedures offers much to the analytical chemist. A further advantage of the extraction method over the widely used precipitation method lies in the cleaner separations that can be achieved by the former. With the later method contamination of precipitates by co-precipitation phenomena is a decided limitation which is minimized only with difficulty, whereas the analog of co-precipitation, i.e., co-extraction, is almost unknown in solvent extraction.

In analytical applications, solvent extraction may serve the following three purposes:

- i) Pre-concentration of trace elements

- ii) Elimination of matrix interference
- iii) Differentiation of chemical species.

Solvent extraction or liquid-liquid extraction by high molecular weight organic amines has become increasingly popular in recent years in studying metal complexes. Extraction by these organic amines combines many of the advantages of both solvent extraction and ion exchange. The main interest of metal extraction by the high molecular weight amines lies in their selectivity towards anionic metal complexes, reversibly formed in an aqueous solution. Hence they are generally referred to as “liquid anion exchangers”. The extent of extraction by the organic bases depends on their nature, structure, size, concentration and the nature of the organic solvent used as diluent

. 1) The solubility of primary long chain amines in non-polar solvents increases with increasing chain length, secondary amines are generally highly soluble in non-polar solvents and sparingly soluble in highly polar solvents. Tertiary amines are completely miscible with non-polar solvents at room temperature and sparingly soluble in polar solvents.

2) Extractive power of the alkylamines generally increases from primary to secondary to tertiary to quaternary amines. The trend may be exceptionally changed if there is extraction by bulky amines, where steric factor play an important role.

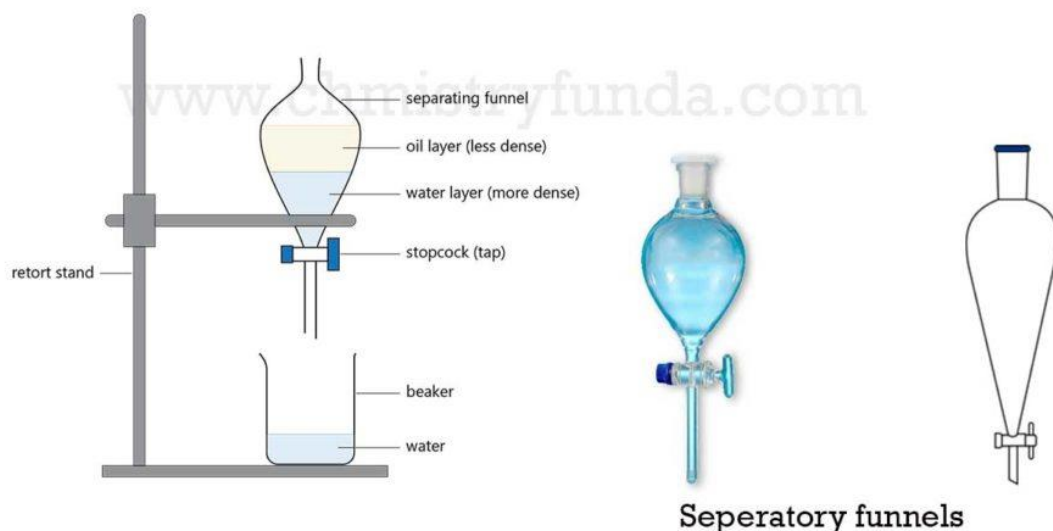
3) Third phase formation :

- a) The third phase formation, a second organic one, is more common in systems where the diluent is an aliphatic hydrocarbon. Aromatic and some derivatives of aliphatic hydrocarbons show the phenomenon usually at high organic phase loading.
- b) The splitting of organic phase is less common, when straight chain alkylamines are used.
- c) Formation of third phase is most common, characteristic of amine sulphate systems.

The compatibility increases in the order:

sulphate > bisulphate > chloride > nitrate.

- d) The formation of the third phase is temperature dependant.



Solvent Extraction:

Solvent Extraction is a separation method in which a solution (usually aqueous) comes into contact with a second solvent (usually organic) that is immiscible with the first to pass the solvent into the second solvent.

This occurs through the partitioning process, which involves the distribution of a solute between two immiscible liquid phases. This technique is called solvent extraction and also known as liquid-liquid extraction.

Principle of solvent extraction:

An extractant, is a substance primarily responsible for the transfer of a solute (here metal) from one phase to the other. The extractant is dissolved in a suitable diluent and together act as a solvent. The diluent is immiscible with other phase which is usually water. The extractant

reacts with the solute by solvation/chelation/ion pair formation etc to extract from the aqueous phase. The distribution equilibrium between two phases is governed by Gibbs phase rule, given by

$$P+V=C+2 \quad (1)$$

Where, P = is the number of phases,

V = is the variance or degree of freedom and

C = is the number of components.

In solvent extraction, we have P=2 two phases namely aqueous and organic phase, the component C=1, viz. solute, in solvent and water phase and at constant temperature and pressure P=1, thus, we therefore have

$$2+1=1+2 \text{ i.e. } P+V=C+2 \quad (2)$$

According to Nernst distribution law,

If $[X]_1$ is concentration of solute in phase 1 and $[X]_2$ is the concentration of solute in phase 2 at equilibrium:

$$K_D = [X]_1 / [X]_2 \quad (3)$$

Where K D is called as the partition coefficient, this partition or distribution coefficient is independent of the total solute concentration in either of the phases. In the above expression for K_D, we have not considered the activity coefficient of the species in the organic as well

as in the aqueous phase. We, therefore, use the term distribution ratio (D) to account for the total concentration of species in the two phases.

Factors affecting on the solvent extraction:

1: Salting out agents:

The extraction of metals may enhance by adding high concentrations of inorganic salts to the aqueous phase. This process is known as salting out effect.

2: pH Value:

The process of the liquid extraction is largely influence by the pH. At the difference pH level, the two metals can be removed.

3: Oxidation state;

The selectivity of the extraction may be sometimes increased by modifying the oxidation state of metal.

For example, extraction of Fe from chloride solution can be prevent by reducing Fe(III) to Fe(II) which does not extract.

4: Masking agents;

These agents which are metal complexing agent, prevent particular metals from taking part in their usual reactions and in this way they remove their interference without requiring an actual separation.

For example, Aluminium can be extract in the presence of iron with 8-quinolinol by masking the iron with an alkali cyanide to form stable ferrocyanide ion. Cyanide, tartrate and EDTA are commonly use as masking agents.

5: Modifier:

Modifiers are the additives to the organic phase to increase the solubility of the extractant in diluent. Example of modifiers is alcohol with high molecular weight.

6: Synergistic agent:

The Synergistic agents are added to the organic phase, in order to enhance the extraction. They form complexes, which taken up by the extract-ant. Neutral organophosphorous compounds added to acidic organophosphours compound exert synergistic effect.

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